

Electric field effect on BiFeO₃ single crystal investigated by Raman spectroscopy

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(Dated: February 2, 2008)

Abstract

Micro-Raman spectroscopy has been used to study lattice dynamics associated with the ferroelectric domains of a BiFeO₃ single crystal at low temperature. The phonon assignment shows a large frequency splitting between the transverse and longitudinal components of the A₁ phonon mode related to the Bi-O bonds in contrast with thin films where the splitting is negligible. Applying an external electric field induces frequency shifts of the low energy modes related to the Bi-O bonds. These softenings are due to a tensile stress via the piezoelectric effect. We give estimates of the phonon deformation potentials.

PACS numbers: 77.80.Bh, 75.50.Ee, 75.25.+z, 78.30.Hv

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Multiferroics have been of particular interest for understanding the fundamental aspects of the mechanism that gives rise to magneto-ferroelectric coupling, as well as for developing devices including spintronics, electro-optics and data storage.[1] BiFeO₃ (BFO) is an attractive and intriguing material because it exhibits both ferroelectric and antiferromagnetic orders at room temperature. First observed in thin films[2], a strong ferroelectric polarization is also now measured in single crystal.[3, 4]

The polarized domain structures in single crystal ferroelectric materials could be an obstacle for devices. Indeed, the dielectric and electromechanical properties are very sensitive to the ferroelectric domains which depend on an external electric field or mechanical stress.[5] The electric field effects on the ferroelectric properties of BiFeO₃ is a topic of current interest.[6]

Despite an intense study of BFO thin films, Raman measurements remain scarce [7, 8] especially on single crystal [9]. The first step needed to understand the ferroelectricity is to investigate the lattice dynamic. It plays a key role in the coupling between the ferroelectric and magnetic orders and its behavior under stress or an applied electric field[10].

In this letter, we report polarized micro-Raman measurements on ferroelectric domains in BiFeO₃ single crystal at 4 K. We have assigned the vibrationnal modes and investigated in a reversible way the structural changes induced by the application of an external electric field.

BiFeO₃ single crystals were grown in air using a Bi₂O₃-Fe₂O₃ flux technique.[3] The as-grown crystals are millimetre sized black platelets. Electron microprobe analysis confirms the stoichiometry of BiFeO₃. The mean thickness of the analysed crystals is 10 μ m. BiFeO₃ single crystal is a ferroelectric with a Curie temperature, $T_c \sim 1100$ K, and shows antiferromagnetic order below the Néel temperature, $T_N \sim 640$ K.[11, 12] In its ferroelectric phase, BFO has a rhombohedrally distorted perovskite structure with the space group R3c and lattice constants $a_{hex} = 5.571 \text{ \AA}$ and $c_{hex} = 13.868 \text{ \AA}$ at room temperature.[13] The spontaneous polarization is along one of the pseudo-cubic [111] directions with a value between 50 and 100 $\mu\text{C}/\text{cm}^2$. [3]. The orientation of the crystal axes has been determined by X-Ray analysis.[3, 4] BFO presents a G-type antiferromagnetic structure with a long range modulation associated with a cycloidal spiral.[14]

Micro and macro Raman measurements have been performed with a laser spot size of 1 μm and 100 μm , respectively [15]. We have used the 514.5 nm (2.41 eV) excitation line

from a $\text{Ar}^+ - \text{Kr}^+$ mixed gas laser. The Raman scattering spectra were recorded at 10 and 300 K using a triple spectrometer Jobin Yvon T64000. The spectrometer was in subtractive configuration with a resolution of 0.1 cm^{-1} in order to detect the electrical field effects on phonon modes. The electrical field has been applied along the z-axis of the crystal using top and bottom ohmic contacts formed by depositing indium drops to the sample, and annealing the sample at 240°C for 10 min.

Figure 1 shows polarized spectra at 10 K obtained from the two different ferroelectric domains in $Z(\text{XX})\bar{Z}$ and $Z(\text{XY})\bar{Z}$ micro Raman geometries.[16] The (a),(b) spectra and (c), (d) ones are related to two different ferroelectric domains. Domains have been visually selected by polarized light. The contrast between bright domains (which correspond to a direction of the spontaneous polarization) and dark domains (which correspond to another one) comes from the birefringence property of the crystal.

Let us focus first on the lattice dynamics. The vibrational modes detected by Raman spectroscopy depend on i) the crystal symmetry which controls the matrix elements of the Raman tensor and ii) the incident and scattered light polarizations which stress the Raman tensor. Group theory predicts 13 Raman active phonons: $\Gamma = 4A_1 + 9E$. All the measurements have been performed in backscattering configuration (incident wave vector parallel to the scattered one). In order to get the pure E modes we have used crossed polarization along the x and y directions, this corresponds to $Z(\text{XY})\bar{Z}$ geometry. The $A_1 + E$ modes have been obtained using parallel polarizations along the x direction. This corresponds to the $Z(\text{XX})\bar{Z}$ geometry. In this scattering geometry, the propagation vector of the relevant phonon is along the Z direction which is parallel to the principal [111] polar axis. The eigenvectors of the A_1 normal mode are parallel to the Z direction whereas those of the E mode are along X and Y directions. The relevant A_1 -symmetry phonons are therefore longitudinal optic (LO) while the E-symmetry phonons are transverse optic (TO). A clear assignement of the Raman modes to a specific bond motion is still missing. An attempt in thin films has concluded that Bi-O bonds contribute mostly to A_1 modes, first and second-order E(TO) modes and Fe-O bonds to third and fourth-order E(TO) modes.[7] The changes from $Z(\text{XY})\bar{Z}$ to $Z(\text{XX})\bar{Z}$ configurations should lead to an enhancement of the A_1 mode intensities in an opposite way of the E modes. There is no ambiguity about the four A_1 modes (145, 175.5, 222.7 and 471 cm^{-1}) and eight out of nine E modes (132, 263, 276, 295, 348, 370, 441, 523 cm^{-1}).[7, 8, 17] The peak at 550 cm^{-1} is only observed with a strong

signal in one ferroelectric domain and in parallel configuration [Fig. 1(b)]. We assigned this peak to the TO forbidden vibrational mode of the the fourth A_1 mode. This assumption is supported by the observation of a peak centered around 1100 cm^{-1} associated with the 2TO line.

We note that a negligible LO-TO splitting of A_1 modes has been observed in thin films [8] and has been interpreted as the domination of the short-range interatomic force over the long-range ionic force. However a giant LO-TO splitting in perovskite ferroelectrics has been measured and discussed in Ref. [18] and especially for BFO in Ref. [19]. The observe splitting comes from a strong Coulomb interaction and a high sensitivity of the ferroelectricity to the domain structure. A small LO-TO splitting thus appears to be a thin film property, in contrast with the large one observed in our measurement on single crystals. A clear understanding of the LO-TO splitting and phonon assignement need more theoretical contributions via ab-initio calculations.[19].

In our case, we observe only the $A_1(\text{TO})$ mode in a ferroelectric domain [peak at 550 cm^{-1} in (b) spectrum of Fig. 1] which is three times larger than the spot diameter. One possible origin of the observation of the $A_1(\text{TO})$ mode is the local symmetry breaking due to strain fields of the domain walls which extend inside the domain making the Raman-forbidden phonons active.

The peaks at 75 and 81 cm^{-1} [in spectra (a), (c) and (b), (d) of Fig. 1, respectively] have been assigned to the last missing E mode. In particular, no enhancement of their intensity is observed as one goes from the parallel to the cross polarizations in contrast to the A_1 modes. The mode at 81 cm^{-1} is detected in $Z(\bar{X}X)\bar{Z}$ configuration and is assigned to the first-order E(LO) mode. The mode at 75 cm^{-1} corresponds to the first-order E(TO) mode. Our assignment is in good agreement with the two modes at the same fequencies observed by infrared measurements on BiFeO3 ceramics.[20] Our samples are pure and no phonon modes associated with impurity phases (Bi_2O_3 , Fe_2O_3 , Fe_3O_4 , ...) have been detected. The Raman peak assignment is summarized in Table I. Singh et al. 8 have reported on BFO films, similar vibrational modes around identical frequencies: E(TO) modes at 275 , 335 , 363 , 456 and 549 cm^{-1} and $A_1(\text{LO})$ modes at 136 , 168 and 212 cm^{-1} . In the present work, we have observed all the modes predicted by the group theory.

Figure 2(a) presents the Raman spectra at 300 K in the range of the first-order E(TO) and E(LO) modes recorded for different voltages of the external applied field. No frequency

shift has been observed for the other vibration modes mainly due to their natural Full Width at Half Maximum at room temperature. The spectra are unpolarized in order to observe the two modes. The applied voltage is raised up to 500 V which represents a field of 5.10^7V/m . Based on a short-range force constant model, calculations have shown the contribution of the Bi-O bonds in the first-order E(TO) modes.[8] In Fig. 2(b), the observed frequency shifts of these peaks are reversible under the applied electric field and saturates for a voltage over 500V. The reversibility of the frequency shift is only observed for around 5 operation cycles before the breakdown of the sample resistance.

The phonon frequency shift of the the first-order E(TO) points out the piezoelectric strain/stress caused by the applied electrical field. The softening of theses peaks is due to tensile stress leading to the expansion of the crystal. According to the theory of Raman spectroscopy[21, 22], the Raman shift of the E modes is related to the strain ϵ_{ij} via phonon deformation potentials α , β and γ

$$\Delta\omega_E = \alpha(\epsilon_{xx} + \epsilon_{yy}) + \beta\epsilon_{zz} + \gamma[(\epsilon_{xx} - \epsilon_{yy})^2]^{1/2} \quad (1)$$

where ϵ_{xx} , ϵ_{yy} and ϵ_{zz} are the normal strains on the plane of trigonal crystal and in the c-axis direction, respectively. For simplicity, we assume that BFO can be described by a trigonal structure and that no x-y strain is generated by the electric field applied along the z axis. The contribution to phonon frequency of the x-y strain has thus been neglected in Eq. 1. The observed shift in the phonon frequency is then related to the distribution of the E_z field across the crystal using the phonon deformation potential β . Unfortunately, this potential is not known. Nevertheless, the electrical field along the z axis can be related to the strain $\epsilon_{zz} = d_{33}E_z$ in a simplified way using the linear piezoelectric coefficient d_{33} . [23] Taking the value for thin films reported in Ref. 2, the corresponding strain ϵ_{zz} from the E_z field is 3.10^{-3} for 500 V. To get a Raman shift of 0.6 cm^{-1} , the phonon deformation potential associated with the E(TO) at 70 cm^{-1} is $-200 \text{ cm}^{-1}/\text{strain unit}$. This value is in the range of the ones obtained for typical piezoelectrics.[21] Using a measured or a calculated value of β , it is possible to determine d_{33} in the same way. ne can notice that the piezoelectric response can be also determined by the phonon frequencies.[24] In Fig. 2(b), a reversible increase of the peak FWHM with voltage is observed. The broadening of the peaks indicates that the induced distorsion of the Bi-O bond is not constant along the penetration depth of the Raman probe probably due to the inhomogeneity of the applied electric field in the sample.

In summary, our measurements reveal a large TO-LO splitting in BiFeO₃ single crystal that is not observed in BiFeO₃ thin films. An applied electric field induces a frequency shift of the Bi-O bonds. This shift is related to the tensile stress due to the piezoelectric effect and allows us to estimate the phonon deformation potentials and the linear piezoelectric coefficient d_{33} .

The authors would like to thank A. Sacuto and Y. Gallais for enlightening discussions and for a critical reading of the manuscript.

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TABLE I: A_1 and E modes for BiFeO_3 single crystal.

| Frequency (cm^{-1}) | Assignment | Frequency (cm^{-1}) | Assignment |
|-----------------------------------|------------|-----------------------------------|------------|
| 75 | E (TO) | 295 | E (TO) |
| 81 | E (LO) | 348 | E (TO) |
| 132 | E (TO) | 370 | E (TO) |
| 145 | A_1 (LO) | 441 | E (TO) |
| 175.5 | A_1 (LO) | 471 | A_1 (LO) |
| 222.7 | A_1 (LO) | 523 | E (TO) |
| 263 | E (TO) | 550 | A_1 (TO) |
| 276 | E (TO) | | |

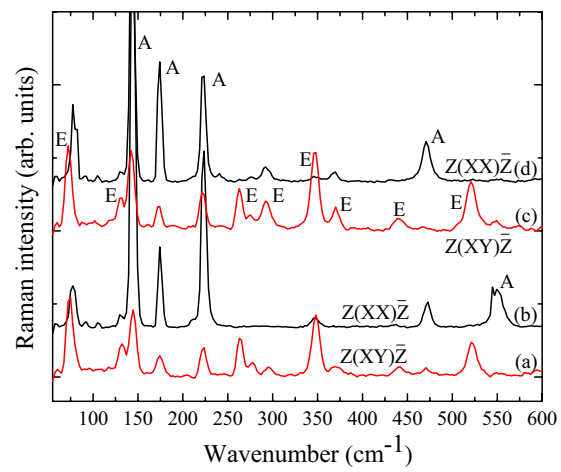


Figure 1 Cazayous et al.

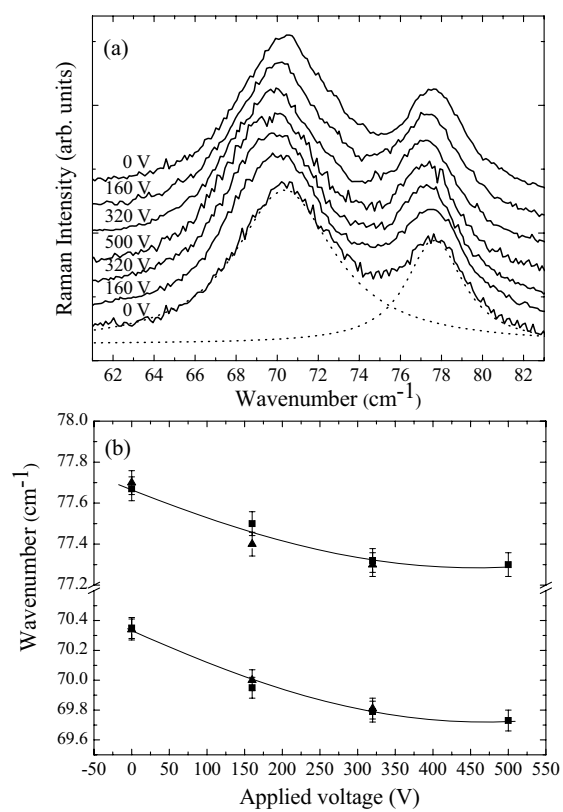


Figure 2 Cazayous et al.